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tert-Butyl Tetraethylphosphorodiamidite in Reactions with α,β-Unsaturated Dicarbonyl Compounds

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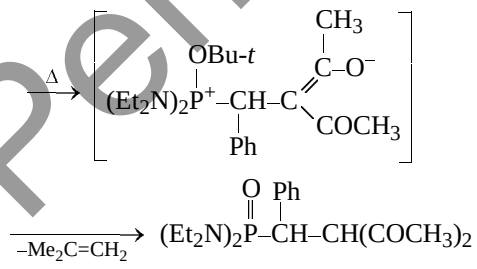
Abstract — Reactions of *tert*-butyl tetraethylphosphorodiamidite with benzylideneacetylacetone, benzylideneacetoacetic ester, and benzylidenemalonic ester are studied. It is shown that the reaction pathway significantly depends on the solvent and temperature. The reaction with benzylidenacetylacetone in ether gives rise to a stable diketophosphonate, while the same reaction in boiling benzene involves elimination of diethylamine and yields a phospholene. The reaction with benzylideneacetoacetic ester proceeds analogously, while with benzylidenemalonic ester the corresponding phospholene is formed exclusively.

It was previously shown that dialkyl hydrogen phosphites and bis(fluoroalkyl) phosphites react with ylidene derivatives of acetylacetone and acetoacetic and malonic esters by way of addition by the C=C bond in the presence of sodium alcoholates as catalysts [1, 2]. Amidoesters of P(III) acids, specifically *tert*-butyl phosphorodiamidite **I**, were not studied in these reactions. We found that these reactions may take different pathways depending on the temperature and solvent and may occur in solvent-free conditions.

The reaction of phosphorodiamidite **I** with benzylideneacetylacetone without solvent occurs with heat release and leads to tarring of the reaction mixture. The reaction performed in dry ether under reflux involves isobutylene evolution (identified as dibromide) and gives 2,2-diacetyl-1-phenylethyl tetraethylphosphonodiamidate (**III**) in high yield. The product is thermally stable and melts without decomposition.

$(Et_2N)_2P–OBu\text{-}t$ + $PhCH=C(COCH_3)_2$

I **II**



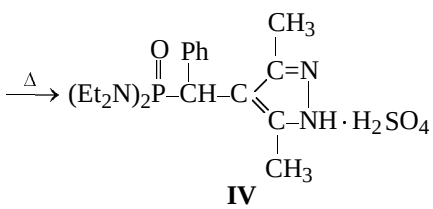
III

The IR spectrum of compound **III** contains absorption bands (ν, cm^{-1}) characteristic of P=O (1180), C=O (1710 and 1720), and PhC=C (1540) groups. The ^1H NMR spectrum shows a triplet at 1.5 ppm (12H, $^3J_{HH}$ 7 Hz) due to the $N–C_2H_5$ methyl protons. The methylene protons give a quartet at 3.46 ppm (8H). The phenyl protons give a singlet at 7.05 ppm (5H), and the $CH_3–C=O$ methyl protons, a singlet at 2.56 ppm (6H).

It is evident that phosphonate **III** undergoes keto-enol tautomerization. This is proved its reaction with copper acetate, leading to formation of copper acetylacetonate as greenish blue crystals, mp 120°C. The structure of phospohonate **III** is also confirmed by its reaction with 2,4-dinitrophenylhydrazine, providing the corresponding phenylhydrazone as reddish orange crystals, mp 127–128°C.

It is known that acetylacetone reacts with hydrazine to give the corresponding pyrazole. We showed that prolonged boiling of phosphonate **III** with hydrazine sulfate gives 3,5-dimethyl-4-(tetraethyldiaminophosphinoylbenzyl)pyrazole sulfate (**IV**).

III + $NH_2–NH_2 \cdot H_2SO_4$



IV

The IR spectrum of product **IV** contains C=C, C=N, P=O, and NH absorption bands at 1620, 1690, 1200, and 3340 cm^{-1}, respectively.

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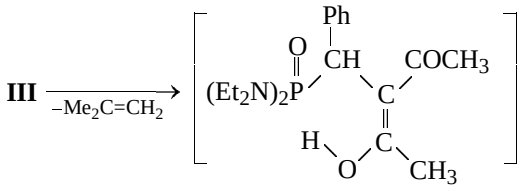
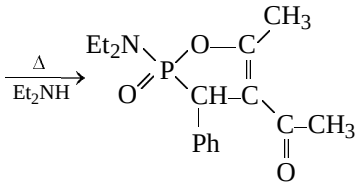
The reaction of phosporodiamidite **I** with benzylideneacetylacetone (**II**) in boiling benzene gives, together with isobutylene, an equimolar amount of diethylamine that distills from the reaction mixture. The latter was identified as hydrochloride (mp 220°C) obtained by passing of dry HCl in the benzene distillate. It is evident that this reaction proceeds through the stage of phosphonate **III** formation, which at elevated temperature cyclizes to 4-acetyl-2-diethylamino-5-methyl-2-phenyl-1,2λ^5-oxaphosph-4-olene 2-oxide (**V**) through enol **III** with Et_2NH elimination.

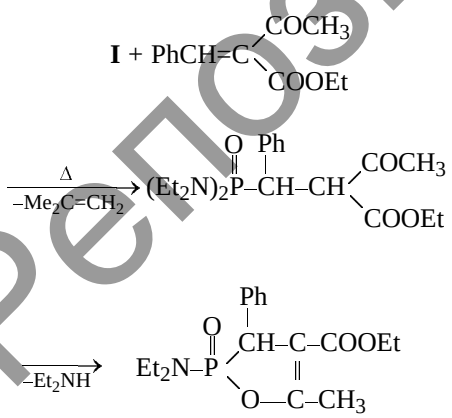




V

Phospholene **V** is a stable white crystalline substance. Its IR spectrum contains bands (ν, cm^{-1}) characteristic of the following groups: P=O (1220), C=C (1620), P–O–C (1010), *s-cis*-C=O (1740), and *s-trans*-C=O (1690).

The reaction of phosphite **I** with benzylideneacetoacetic ester (**VI**) in boiling benzene with simultaneous distillation of diethylamine and evolution of isobutylene yields 2-diethylamino-4-ethoxycarbonyl-5-methyl-3-phenyl-1,2λ^5-oxophosph-4-olene 2-oxide (**VII**).

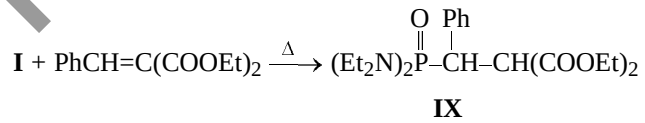


VII

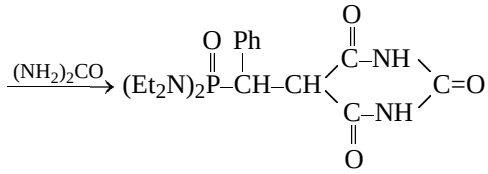
The IR spectrum of compound **VII** in the carbonyl absorption region has a complicated pattern associated with rotational isomerism in the C=C–COOEt fragment (1710–1740 cm^{-1}). Bands of the C=C, P=O, and P–O–P groups are also observed at 1640, 1210, and 1020 cm^{-1}, respectively.

Note that in going from benzylideneacetoacetic ester to benzylidenemalonic ester (**VIII**) linear products no longer tend to cyclize to corresponding phospholenes. This fact agrees with the proposed scheme, according to which the cyclization proceeds through the enolic form whose formation is impossible in the case of benzylidenemalonic ester. The same scheme was earlier proposed by Pudovik and Moshkina [2]. The reaction of compound **I** with benzylidenemalonic ester (**VIII**) upon prolonged boiling in benzene or dioxane or within 0.5–1 h in CH_2Cl_2 yields diethyl (tetraethyldiaminophosphinoylbenzyl)malonate (**IX**). The latter was isolated as a yellow oil which was purified by column chromatography on silica gel. The IR spectrum of compound **IX** shows bands characteristic of P=O (1200 cm^{-1}) and C=O (1720, 1745 cm^{-1}) groups.

The synthesized (tetraethyldiaminophosphinoylbenzyl)malonic esters were used for preparing the corresponding barbituric derivatives. The synthesis was carried out by a conventional synthetic procedure for barbituric acids by heating the former in ethanol with carbamide in the presence of RONa. As a result, (tetraethyldiaminophosphinoylbenzyl)barbituric acid **X** was isolated.



IX



X

The IR spectrum of compound **X** contains absorption bands at 1705 and 1720 cm^{-1}, a broadened band of the OH group at 3180 cm^{-1}, a band of the NH group at 3340 cm^{-1}, and a band of the P=O group at 1180 cm^{-1}.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-75 spectrometer in the range of 400–4000 cm^{-1} for KBr pellets. The ^{1}H NMR spectra were obtained on a Tesla BS-587 spectrometer (80 MHz) in C_6D_6 and D_2O

against internal HMDS. The melting points were measured on a Boetius hot stage.

Reaction of *tert*-butyl tetraethylphosphorodiamidite (I) with benzylideneacetylacetone (II) in ether. Compound **I**, 5.0 g, compound **II**, 3.8 g, and 50 ml of dry ether were placed in a round-bottom flask and heated to boil. Vigourous isobutylene evolution (370 ml, 83%) was observed. After the gas evolution had been complete, the solvent was removed, and the residue crystallized. It was treated with hexane to obtain 2,2-diacetyl-1-phenylethyl tetraethylphosphonodiamidate (**III**) as needle-like crystals. Yield 5.4 g (72%), mp 140–141°C. Found, %: C 63.48; H 8.92; N 7.42; P 8.34. $C_{20}H_{33}N_2O_3P$. Calculated, %: C 63.16, H 8.68; N 7.37; P 8.16.

Reaction of phosphonodiamidate III with hydrazine sulfate. A mixture of 4.8 g of compound **III** and 2.6 g of hydrazine sulfate was refluxed for 3–4 h in 25 ml of absolute alcohol. The reaction progress was controlled by TLC. The solvent was removed, and the residue was crystallized from benzene to obtain 4.1 g (58%) of 3,5-dimethyl-4-(tetraethyldiaminophosphinoylbenzyl)pyrazole sulfate (**IV**), mp 293°C. Found, %: C 33.63; H 9.45; N 15.98; P 8.86; S 8.96. $C_{20}H_{34}N_4O_5PS$. Calculated, %: C 33.99; H 9.63; N 15.86; P 8.78; S 9.06.

Reaction of phosphorodiamidite I with benzylideneacetylacetone (II) in benzene. Compound **I**, 5.0 g, and 3.8 g of compound **II** were refluxed in 50 ml of benzene. Vigorous isobutylene evolution (395 ml, 88%) was observed. After the gas evolution had been complete, the benzene was distilled off together with the diethylamine formed. The latter was identified as hydrochloride obtained by passing dry HCl through the distillate, yield 1.9 g (87%), mp 220°C. The residue after removal of benzene was crystallized from a benzene–hexane mixture to obtain 4-acetyl-2-diethylamino-5-methyl-2-phenyl-1,2λ^5-oxaphosph-4-olene 2-oxide (**V**). Yield 4.1 g (67%), mp 124–125°C. Found, %: C 62.21, H 7.48; N 4.24; P 10.32. $C_{16}H_{22}NO_3P$. Calculated,%: C 62.54; H 7.17; N 4.56; P 10.09.

Reaction of phosphorodiamidite I with benzylidenacetoacetic ester (VI). A mixture of 5.0 g of compound **I** and 4.4 g of compound **VI** was refluxed in 50 ml of benzene. Isobutylene, 360 ml, and 1.6 g (74%) of diethylamine hydrochloride were isolated. The remaining reaction mixture was treated with dry ether to obtain 2-diethylamino-4-ethoxycarbonyl-5-methyl-3-phenyl-1,2λ^5-oxophosph-4-olene 2-oxide (**VII**) as white crystals. Yield 4.6 g (68%), mp 120–121°C. Found, %: C 60.28; H 7.43; N 4.51; P 8.81. $C_{17}H_{24}NO_4P$. Calculated, %: C 60.53; H 7.12; N 4.15; P 9.19.

Reaction of phosphorodiamidite I with benzylidenemalonic ester (VIII). A mixture of 5.0 g of compound **I** and 5.0 g of compound **VIII** was refluxed in 50 ml of benzene or dioxane for 3–4 h or in methylene chloride for 0.5–1 h. The reaction progress was controlled by TLC. The solvent was removed to leave a light yellow oil that decomposed on distillation. The oil was subjected to column chromatography on silica gel (eluent benzene–hexane, 1 : 1) to isolate diethyl (tetraethyldiaminophosphinoylbenzyl)malonate (**IX**). Yield 4.7 g (54%). Found, %: C 59.65; H 7.44; N 6.12; P 7.48. $C_{22}H_{37}N_2O_5P$. Calculated, %: C 60.00; H 8.41; N 6.36; P 7.05.

Reaction of phosphonodiamidate IX with carbamide. To a solution of sodium ethylate prepared from 0.7 g of sodium in 30 ml of absolute ethanol, 4.2 g of carbamide and 4.4 g of compound **IX** were added. The reaction mixture was refluxed for 6–7 h, sodium barbiturate precipitated and was dissolved in water. The solution was acidified with HCl, filtered, and concentrated in a vacuum. (Tetraethyldiaminophosphinoylbenzyl)barbituric acid precipitated and was recrystallized from ethanol. Yield 2.1 g (52%), mp 156°C. Found, %: C 55.28; H 7.48; N 13.51; P 7.33. $C_{19}H_{29}N_4O_4P$. Calculated, %: C 55.88; H 7.11; N 13.73; P 7.60.

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